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by

K. Kim, L.B. Lin, J.M. Ginder, T.L. Gustafson and A.J. Epstein

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University of Pennsylvania
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PHOTOLUMINESCENCE AND PICOSECOND PHOTOINDUCED ABSORPTION OF POLYANILINE

K. KIM, L. B. LIN, J. M. GINDER*, T. L. GUSTAFSON, and A. J. EPSTEIN
Department of Physics and Department of Chemistry, The Ohio State University
Columbus, OH 43210-1106 (U.S.A.)

ABSTRACT

The photoluminescence and photoinduced absorption are reported for leucoemeraldine and emeraldine forms of polyaniline in the picosecond to nanosecond time domain. The importance of bond vibration, charge tunneling and ring rotations in varying relaxation processes is determined. The temperature dependence of the photoluminescence decay time of the leucoemeraldine base dissolved in N-methyl pyrrolidinone is reported. The decay time decreases as the temperature increases. From the Arrhenius plot, the activation energy is estimated to be ~ 0.1 eV. These data suggest that backbone vibrations dominate this photoluminescence decay mechanism. From the comparison of the result to that of the monomer, aniline, it is concluded that a polaron-exciton confined in the basic unit including a ring and adjacent nitrogen atoms is responsible for the photoluminescence. The picosecond photoinduced absorption of emeraldine base films optically pumped at 2.1 eV and probed at 1.5 eV and 2.9 eV are compared with the previously measured picosecond photoinduced bleaching probed at 2.0 eV. While all three of them show initial fast decay, the photoinduced absorption at 1.5 eV does not show a substantial residue on the nanosecond time scale. This is in contrast to the photoinduced bleaching at 2.0 eV and 2.9 eV photoinduced absorption for which more than half of the signal remains even after a few nanoseconds. Preliminary measurements of emeraldine base films at a probe energy of 2.9 eV indicate that the decay slows down when the temperature is lowered. For emeraldine base in N-methyl pyrrolidinone solution, this long lived tail in picosecond photoinduced absorption disappears. These data strongly suggest the importance of the ring-torsion or interchain processes in the excitation decay mechanism of the 2.9 eV photoinduced (polaron) absorption.

INTRODUCTION

Though many of the early introduced conducting polymers, like polyacetylene and polythiophene, have carbon backbones that are responsible for the major electronic properties [1], polyaniline is made up of phenyl rings connected by nitrogen atoms, with (amine) or without (imine) hydrogen atoms. Polyaniline has three different oxidation states, fully reduced leucoemeraldine base (LEB), partially oxidized emeraldine base (EB), and fully oxidized pernigraniline base (PNB), as shown schematically in Fig. 1.

The lowest energy direct optical absorption peak of aniline is at ~ 4.3 eV [2] while that of its polymeric form, LEB, is at 3.8 eV.[3] When polyaniline is not fully reduced there appears another optical absorption peak within the visible range. EB has absorption peaks at 2.0 eV and 3.8 eV. The 3.8 eV peak is assigned to π - π^* band-gap absorption, while the 2.0 eV peak is interpreted as the result of a charge transfer exciton-like transition from the benzenoid rings to the quinoid rings.[3, 4] PNB has optical absorption peaks at 2.3, 3.8, and 4.3 eV with the first

*Present address: Scientific Research Lab., Ford Motor Co., Dearborn, MI 48121

absorption being attributed to excitations across a Peierls gap and the others higher energy π - π^* transitions.[5]

Near-steady-state photoinduced absorption (PA) studies of EB revealed peaks at 1.4 eV and 2.0 eV that were assigned to ring-torsional polarons.[3, 4, 6] The EB charge transfer exciton picosecond photoinduced bleaching (PB) was earlier reported.[7] It was shown that, for decay time less than a few nanoseconds, the PB decay curve could be fit to a power law, $\sim t^{-0.11}$; the decay was independent of temperature, suggesting tunneling as the primary decay mechanism. The presence of photoluminescence (PL) in LEB and the reduction of its intensity with oxidation (introduction of quinoid groups) has been noted.[8-10] We report here the temperature dependence of the PL decay time of LEB in solution and the fast relaxation behavior of the polarons in EB. We determine that there are important roles for bond vibration, ring rotation and tunneling in determining the relaxations in the polyanilines.

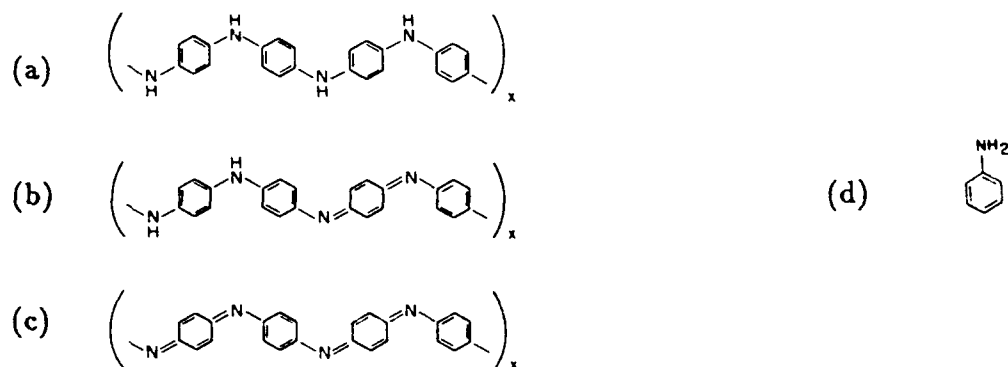


Fig. 1 Schematic illustration of aniline and the three stable oxidation states of polyaniline. (a) leucoemeraldine base (LEB), (b) emeraldine base (EB), (c) pernigraniline base (PNB), (d) aniline.

EXPERIMENTAL TECHNIQUES

Polyaniline (emeraldine hydrochloride salt) powder was obtained by polymerization of aniline in 1M HCl solution using ammonium peroxydisulfate as the oxidizing agent. It was subsequently converted to the emeraldine base form by treatment with ammonium hydroxide.[11] To obtain a solution of reduced LEB, EB was dissolved in N-methyl pyrrolidinone (NMP) and reduced by hydrazine hydrate.[12] The reduction was confirmed by the disappearance of the optical absorption peak at ~ 2 eV. The LEB in NMP was optically pumped by the frequency doubled Rhodamine 6 G dye laser pulse (4.2 eV, 10 ps) and the resultant luminescence was monitored by a Hamamatsu type R928 photomultiplier tube connected to a EG&G model 4400 boxcar averager. The decay time was obtained by the convolution of the impulse response of the measuring system, under the assumption of a single exponential decay.[2]

Two different picosecond PA measurement systems were used for the study of picosecond PA of EB films, for probe energies of 1.5 eV and 2.9 eV. Each system was made up of two cavity-dumped dye lasers synchronously pumped by a mode-locked and frequency doubled or tripled Nd:YAG laser. One dye laser pulse optically pumps the sample, the other laser pulse is delayed a set time, and its intensity after passing through the sample is measured. The temperature dependence of the 2.9 eV picosecond PA was studied for EB films. The room temperature dynamics of the 2.9 eV PA were compared for film and solution samples of EB.

RESULTS

Figure 2 (a) shows the temperature dependence of the PL decay time under the assumption of single exponential decay for LEB in NMP. As the temperature increases, the decay time increases. The PL emission starts at the absorption edge ~ 3.2 eV and peaks at ~ 2.9 eV.[8-10] A low pass optical filter was used to block the emission spectrum for energies greater than ~ 3.65 eV (wavelength less than ~ 420 nm). The result is compared to the full spectrum in Fig. 2. Within the experimental error, no significant differences are found. The characteristic decay time, $\tau \sim 1.5$ ns at room temperature, i.e., shorter than that of aniline solution, which has a solvent independent decay time of 3.1 to 3.4 ns.[2] In Fig. 2 (b), the activation energy, Δ , for τ is obtained from an Arrhenius plot ($\tau \propto \exp(-\Delta/k_B T)$); the activation energy is estimated to be 0.084 eV and 0.12 eV dependent upon choice of slopes.

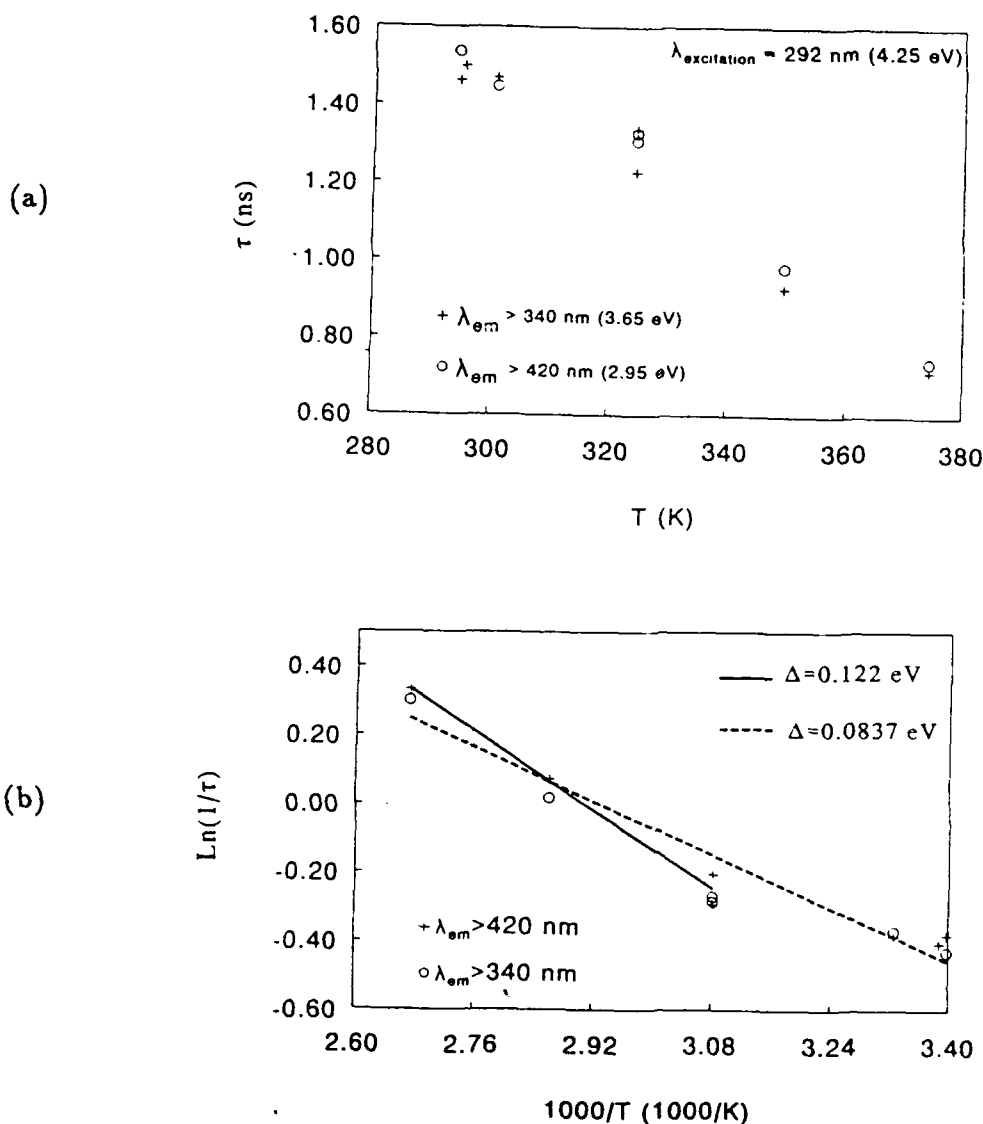


Fig. 2 (a) The temperature dependence of photoluminescence decay time for leucoemeraldine polymer in NMP solution. The decay time was obtained under the assumption of single exponential decay. (b) An Arrhenius plot fitting all τ data points gives an activation energy $\Delta = 0.084$ eV (broken line), exclusion of the lowest temperature data points yields $\Delta = 0.12$ eV (solid line).

Figure 3 compares the room temperature EB film picosecond PA data probed at 1.5 and 2.9 eV to the previously reported [4] PB at 2.0 eV. In each case the pump energy was 2.1 eV. The rise time difference comes from the resolution of the measurement systems. The actual rise time is below the resolution of the experiments. The 1.5 eV PA decays very rapidly (~ 100 ps), unlike the 2.9 eV PA and 2.0 eV PB curves, about half of whose intensity remains even after a few nanoseconds. Attempts were made to fit the 1.5 eV and 2.9 eV PA curves to various functional forms including single and double exponentials, stretched exponential, and power law, with inconclusive results.

At the probe energy of 2.9 eV, the picosecond PA decay time increased when the temperature was decreased. In contrast, when EB in NMP solution was probed at 2.9 eV, the picosecond PA decay lacked the long tail in nanosecond range.

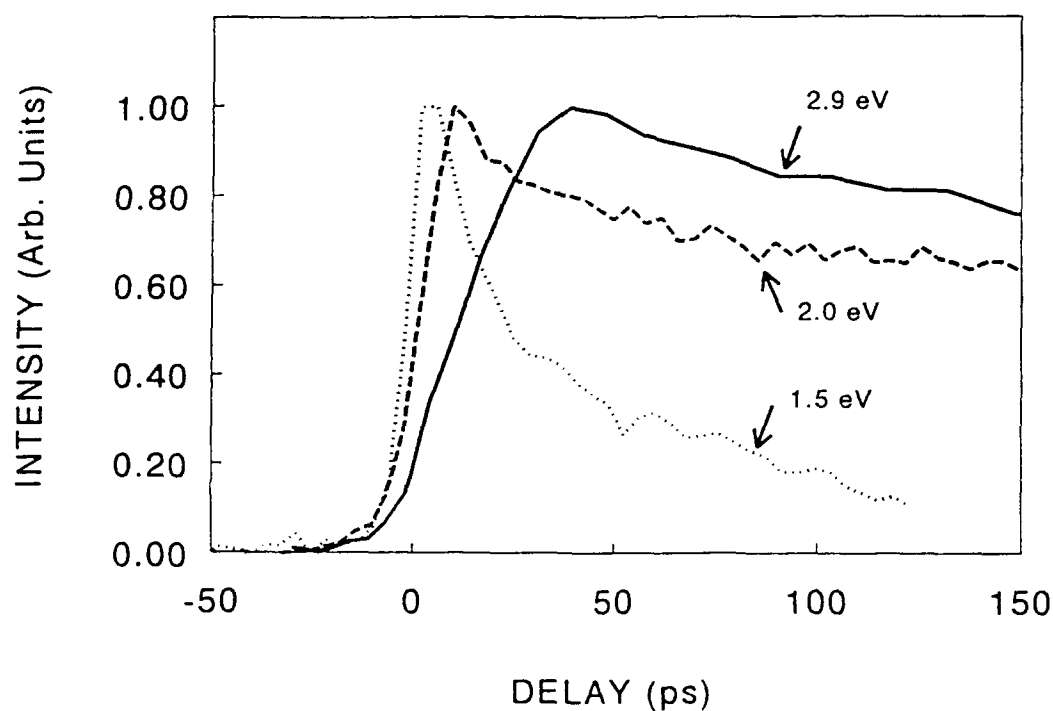


Fig. 3 Normalized picosecond photoinduced absorption of emeraldine base excited at 2.1 eV and probed at 1.5, 2.0, and 2.9 eV. The 2.0 eV signal corresponds to photoinduced bleaching; the 1.5 eV and 2.9 eV signals correspond to photoinduced absorption. The three signals, measured on three different systems, were normalized. The different rise times reflect resolution of each system.

DISCUSSION

The room temperature PL decay time of the LEB in NMP is appreciably shorter than that of aniline solution. This can be explained by the presence of residual quinoid rings present in most LEB.[3, 13] The same temporal behavior below and above the emission peak strongly suggests that only one PL mechanism is involved.[14] Since LEB is a non-degenerate ground-state polymer, the PL emission likely originates from the geminate decay of a polaron-exciton.[15] The PL emission spectrum of LEB in NMP, like that of aniline in solution, has only one peak and does not show any vibrational structure, unlike the PL emission spectra of, for example, polythiophene (PT) or polyphenylenevinylene (PPV).[2, 8-10, 15, 16] The similarity between the PL of aniline [2] and LEB strongly supports the confinement of the excitation to a single ring and adjacent nitrogen

unit. The activation energy for the decay time constant of the PL of LEB in NMP is approximately ten times greater than the estimated ring rotational energy barrier in LEB [6, 13] and is in the range of backbone vibrational energies,[3] suggesting that intra-ring vibrations play an important role in the PL emission. The temperature dependent short time decay of the PL (polaron-exciton decay) is in contrast to the temperature independent PB of the 2.0 eV absorption associated with the charge transfer exciton.[4] That is, the inter-ring charge transfer exciton primarily decays by a temperature independent tunneling process at short times.

While the photoinduced bleaching peak (2.0 eV) and absorption peak (2.9 eV) of EB films have a slowly decaying component, the picosecond PA probed at 1.5 eV decays very rapidly. This corresponds well to the near-steady-state PA results [3] which are sensitive to excitations present to the millisecond time scale. In contrast to the 2.0 eV PB behavior, the picosecond PA at 2.9 eV has a weak temperature dependence, such that the initial decay rate slows down modestly when the temperature is decreased. In addition, the 2.9 eV picosecond PA of EB dissolved in NMP has a very fast decay with no long lived component, unlike the case of EB film. The temperature and environmental variation of the 2.9 eV picosecond PA supports the importance of ring-torsion in the dynamics of photoexcited defects.[6]

SUMMARY

It is shown that the leucoemeraldine base and emeraldine base polymers have a variety of optical responses on the picosecond time scale. From the dynamics and spectra of these excitations and the dependence on chemical structure, it is suggested that the luminescence in leucoemeraldine base arises from a polaron-exciton essentially confined to a single repeat, and whose decay is determined by back bone (intra-ring) vibrations, that the charge transfer exciton in emeraldine base decays at short times primarily by tunneling, and that polaron relaxation in these polymers is controlled primarily by changes in ring-torsion angle (dominated by steric effects). Further studies are in progress to elucidate the interplay of these phenomena.

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